Adsorption Behavior of Alternating Copolymers with Hydrophobic and Hydrophilic Side Chains: An ESR Study of the Spin-Labeled Polymers[†]

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ABSTRACT: The conformation[‡] of the polymers poly(1-octadecene-*alt*-maleic anhydride) (PODMA, **1**) and poly(1-dodecene-*alt*-maleic acid mono{2-[2-[2-[2-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethyl} ester) (PDDMAM(EO)$_7$Me, **2**) adsorbed on Aerosil 200 was evaluated by means of ESR spectroscopy. The fraction of the polymer segments in "trains", "short loops", and "tails"/"long loops" was determined as a function of the degree of surface coverage Θ according to a modification of the method of Sakai et al. The theory of Scheutjens and Fleer fits the experimental results obtained for PODMA very well; the theory fails, however, to predict the experimental results obtained for PDDMAM(EO)$_7$Me. As a consequence the description of the conformation of PDDMAM(EO)$_7$Me in the adsorbed state cannot be described by the present method. The differences in the adsorption behavior of PODMA and PDDMAM(EO)$_7$Me are explained in terms of structural features of the polymers. Interactions of the heptakis(ethylene oxide) side chains of PDDMAM(EO)$_7$Me in the adsorbed state lead to a substantial fraction of segments in "trains" even at high surface coverages.

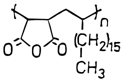
Introduction

In many cases the ultimate properties of materials are achieved by coating with polymers. The surface layer in particular determines evenness and luster, chemical stability, and hardness, but also biocompatibility and flocculation behavior of particles in suspension.[1] The adhesion of the coatings is determined by the interaction between the coating polymer and the coated materials. Therefore the interface has been of particular interest from an applied as well as from a theoretical point of view. A question of basic relevance is what the conformation of the polymers at the very surface looks like. Jenckel and Rumbach applied to the adsorbed polymers the model of "trains", "loops", and "tails".[2] This model is generally accepted, because theoretical predictions fit most experimental results.[3−5]

Experimentally, the fraction of polymers adsorbed as "trains", "loops", and "tails" was determined by means of spectroscopic methods such as IR,[6−11] NMR,[12−14] and ESR spectroscopy.[15−24]

For ESR spectroscopic measurements the presence of an unpaired electron is a prerequisite. Therefore, the polymers are labeled with a stable free radical. Nitroxide spin labels, developed originally for the study of biopolymers, have proved to be the most suitable class of organic radicals to fulfill the requirements of a spin label;[24,25] their ESR spectra reveal quantitative dynamic information.[15,25,26] Since the spin label is covalently linked to the polymer chain, the mobility of the label reflects the mobility of the chain segment. According to the ESR method developed by Robb and Smith,[15] Sakai et al.[19] employed three model spectra to distinguish between differently mobile chain segments: (i) the spectrum of a diluted polymer solution at room temperature is a model for very mobile chain segments as defined by "tails" and "long loops", (ii) the spectrum of a diluted polymer solution at 153 K is a model spectrum for immobilized chain segments as defined by "trains", and (iii) the spectrum of a polymer melt is a model spectrum for partly mobile chain segments as defined by "short loops". The fraction of polymer segments in "tails"/"long loops", "short loops", and "trains" is determined via simulation of a measured spectrum of an adsorbed polymer by weighted summation of the three normalized model spectra.

In the present paper we describe the adsorption behavior of alternating copolymers of 1-octadecene with maleic anhydride (PODMA, **1**) and of 1-dodecene and a maleic acid monoester of heptakis(ethylene oxide) monomethyl ether (PDDMAM(EO)$_7$Me, **2**) on Aerosil 200.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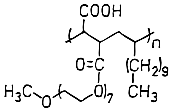
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These copolymers differ from the polymers studied up to now by several structural features: (i) PODMA has, besides the polar anhydride group, an unpolar C_{16} side chain attached to the main chain. (ii) PDDMAM(EO)$_7$Me has a polar and protic carboxylic group, a polar and aprotic heptakis(ethylene oxide) monomethyl ether moiety and an unpolar C_{10} side chain attached to the main chain. In both cases the nitroxide spin labels are attached closely to the main chain; therefore, the ESR spectrum reflects sensitively the difference in the relaxation process of different chain segments in tails, loops, and trains. The conformation of the adsorbed polymer is determined by means of ESR spectroscopic measurements according to the method of Sakai et al.[19] as a function of the degree of surface coverage, Θ. The fraction *p* of polymer segments adsorbed in "trains", as a function of the total amount of adsorbed polymer is compared with the theoretical results obtained by Scheutjens and Fleer (SF theory) based on conforma-

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[†] Dedicated to Professor Dr. Max Herberhold on the occasion of his 60th birthday with best wishes.

[‡] In this work "conformation of polymers" means a macroscopic conformation defined by the mobility of chain segments as in "tails" or "long loops", "short loops", and "trains".

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tional statistics.[5,27] The results of this investigation are expected to give an answer with respect to the range of applicability of the method to linear polymeric structures with long hydrophobic and hydrophilic graftlike side chains. It is to be noted, however, that the location of the spin label and the point of interaction of the macromolecule with the silica surface coincide for PODMA but not for PDDMAM(EO)$_7$Me. This might result in a limitation for the interpretation of the experimental results.

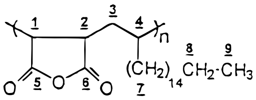
Experimental Section

Reagents. The spin label 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxyl (4-amino-TEMPO) (from Sigma, Germany) and the coupling reagent *N*,*N*′-dicyclohexylcarbodiimide (DCC) (from Fluka, Germany) were used without further purification. Trichloromethane ($CHCl_3$) (stabilized with ca. 1% ethanol) (from Riedel de Häen, Germany) was destabilized by passing over a column packed with basic aluminum oxide (from Fluka, Germany; activity I according to the rules of Brockmann) in an inert atmosphere. Technical dichloromethane (CH_2Cl_2) was freshly distilled over calcium hydride before use. Nitrogen and argon (both from Linde) were passed over molecular sieves (4 Å), finely distributed potassium on aluminum oxide, and reduced Phillips catalyst 800/350 (Cr^{II} on silica gel) for purification.

Aerosil 200 (from Degussa AG) was dried 3 h in vacuo at 300 °C, cooled, and moistened with trichloromethane before treatment with the polymer solution. All operations were performed under vacuum or a blanket of dry inert gas.

Polymers. Poly(1-octadecene-*alt*-maleic anhydride) (PODMA, **1**) (from Polyscience Ltd.) and poly(1-dodecene-*alt*-maleic acid mono{2-[2-[2-[2-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]ethyl} ester) (PDDMAM(EO)$_7$Me, **2**) (from AKZO Chemicals GmbH) were used in the spin-labeling reaction without further purification.

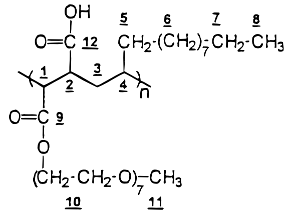
Characterization of the Polymers. PODMA. IR (KBr): 2925, 2853 (C—H stretching frequency); 1859, 1781 (C═O anhydride stretching frequency); 1715 (C═O ester stretching frequency); 1474 (C—H distortion frequency); 1223 (C—O stretching frequency) cm^{-1}. ^1H-NMR (toluene-d_8, 373 K) (s = singlet, b = broad, vb = very broad): δ 0.87 (s, b, 3H, no. 9), 1.26 (s, b, 30H, nos. 8 + 7), 1.97 (s, vb, 1H, no. 4), 2.27 (s, vb, 2H, no. 3), 2.87 (s, vb, 1H, no. 2), 3.20 (s, vb, 1H, no. 1) ppm.



^{13}C-NMR (toluene-d_8, 373 K): δ 14.24 (1C, no. 9), 23.15 (1C, no. 8), 29.90 and 30.37 (14C, no. 7), 173.21 (2C, nos. 5 + 6) ppm (the three CH groups and the CH_2 group of the polymer backbone could not be distinguished from the noise). Anal. Calc for $(C_{22}H_{38}O_3)_n$: C, 75.38; H, 10.93. Found: C, 75.85; H, 10.42. The molar ratio of the monomers was determined to be 1.1:1 by quantitative IR spectroscopy and elemental analysis. GPC analysis: M_w = 40 600; M_n = 22 900; M_w/M_n = 1.8 (according to polystyrene standards).

PDDMAM(EO)$_7$Me. IR (film): 2925, 2856 (C—H stretching frequency); 1767 (C═O anhydride stretching frequency); 1733 (C═O ester and carboxyl stretching frequency); 1469 (C—H distortion frequency); 1255 (C—O ester and carboxyl stretching frequency); 1110 (C—O ether stretching frequency) cm^{-1}. ^1H-NMR (DMSO-d_6, 373 K): δ 0.88 (s, b, 3H, no. 8), 1.17 (s, b, 18H, nos. 5 + 6 + 7), 2.87 (s, 3H, no. 11), 3.15 (s, 28H, no. 10), 12.39 (s, vb, 1H, COOH) (the three CH groups and the CH_2 group of the polymer backbone could not be distinguished from the noise).

^{13}C-NMR (DMSO-d_6, 373 K): δ 13.00 (1C, no. 8), 21.93 (1C, no. 7), 28.41 (7C, no. 6), 30.68 (1C, no. 5), 57.44 (1C, no. 11), 59.97−71.88 (14C, no. 10), 172.87 (2C, nos. 9 + 12) ppm (the three CH groups and the CH_2 group of the polymer backbone could not be distinguished from the noise). Anal. Calc. for $(C_{31}H_{58}O_{11})_n$: C, 61.36; H, 9.63. Found: C, 61.68; H, 9.76. The molar ratio of the monomers was determined to be 1:1 by quantitative IR spectroscopy and elemental analysis. GPC analysis: M_w = 13 200; M_n = 3600; M_w/M_n = 3.7 (according to polystyrene standards).



Spin Labeling of the Polymers. PODMA. A solution of 4 g of polymer (11.5 mmol of repeating units; according to the alternating structure of the polymer the repeating unit is defined as the sequence of the two monomers) in 50 mL of dry $CHCl_3$ was mixed with a solution of 0.027 g (0.16 mmol) of 4-amino-TEMPO in 1 mL of trichloromethane in an inert gas atmosphere. The reaction mixture was stirred at room temperature overnight. The labeled polymer was precipitated in 300 mL of cold methanol (263 K). For purification the polymer was reprecipitated three times from $CHCl_3$ solution in cold methanol and dried in vacuo at room temperature.

The chosen polymer to spin label ratio guarantees a maximum label concentration of one spin label per 290 C atoms of the polymer backbone.

PDDMAM(EO)$_7$Me. A solution of 5 g of polymer (8.25 mmol of repeating units) and 0.028 g of 4-amino-TEMPO (0.17 mmol) in CH_2Cl_2 were mixed with a solution of 0.04 g (1.94 mmol) of DCC at 263 K. After 12 h the insoluble DCH was removed by filtration and the solvent was removed by distillation. The polymer was then dissolved in bidistilled water, unreacted DCC was removed by filtration, and the polymer was isolated by distillation of the water and dried at room temperature in high vacuum.

The chosen polymer to spin label ratio guarantees a maximum label concentration of one spin label per 190 C atoms of the polymer backbone.

For both the polymers the influence of the spin label on the adsorption behavior is negligible, as was shown by the identical adsorption isotherms of labeled and unlabeled polymers.

Measurements. Gel permeation chromatography (GPC) was carried out using an ERC 64 pump with an ERC-7215 UV detector (wavelength 264 nm) and a Waters 410 RI detector. A combination of columns was applied with PL gel from Polymer Laboratories: length of the columns, 300 mm; diameter, 7.5 mm; diameter of the gel particles, 5 μm; pore widths, 100, 500, 10^3, and 10^4 Å. *N*,*N*-Dimethylacetamide (DMAC) with 0.25 wt % LiBr was the eluting solvent with a flow rate of 0.5 mL/min. The column temperature was 355 K. Calibration of the columns was performed with polystyrene standards (from Polymer Standard Service).

^1H- and ^{13}C-NMR spectra were recorded on a Bruker CXP FT-NMR spectrometer at 200 and 50 MHz, respectively. Toluene-d_8 and dimethyl sulfoxide-d_6 were used as solvents, and TMS was used as the internal standard.

Thermogravimetric analyses (TGA) were carried out on a TG 209 with a TA-System-controller TASC 412/2 and kinetic software from Netzsch. The scale had a sensitivity of $\pm 5 \times 10^{-3}$ mg and the weight of the sample was in the range 10−20 mg.

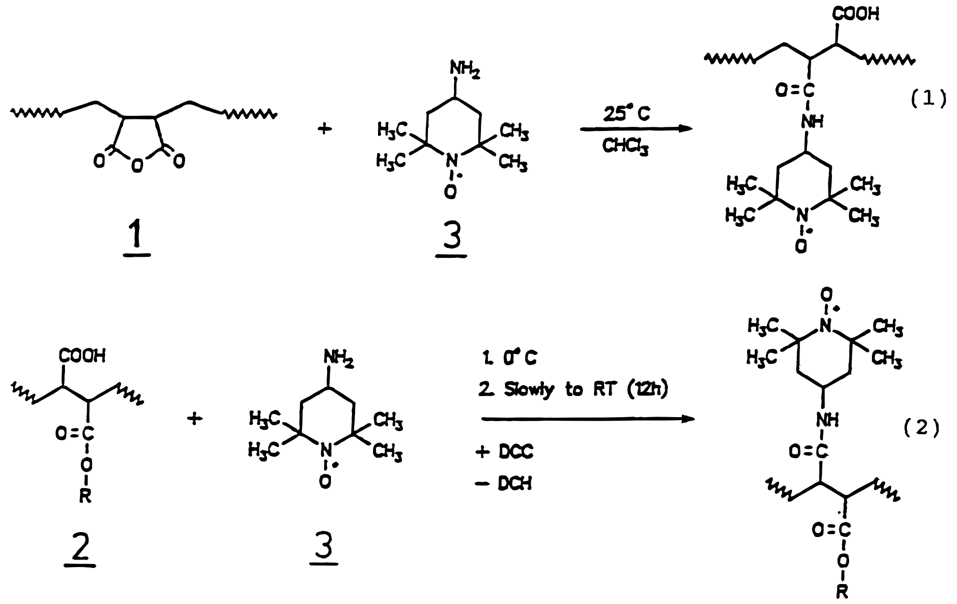
IR measurements were made on a Nicolet FT-IR 510P.

The centrifuge was a Centrikon H-401B (Kontron Instruments).

Elemental analyses were performed with a Carlo-Erba MOD 1106 instrument.

ESR spectra were recorded on a Bruker ER 200 D/ESP 3220 spectrometer. The computer unit had an ESP 300 E configuration. The instrument was equipped with a Bruker variable temperature unit ER 4111 UT, a signal channel, and a field controller ER 023 M, a microwave bridge controller ESP 1600-1048, a DSPD preamplifier E 025, and a Hewlett Packard 5320

Scheme 1



microwave frequency counter. The X-band spectrometer works at 9.7858 GHz at room temperature.

Adsorption Experiments. All adsorption experiments were carried out with the nonporous and pyrogenic silica Aerosil 200 (from DEGUSSA AG, Germany) in a special apparatus described by Killmann.[28-30] The Aerosil 200 was heated for 3 h at 573 K in vacuo (0.03 mbar) to yield a defined number of 2.4–2.5 free silanol groups per 100 Å^2.[31,32] Then the Aerosil was suspended in $CHCl_3$ and a polymer solution in $CHCl_3$ was added. The final concentration of Aerosil was 10 g/L, and the concentration of the polymer varied between 0.1 and 10 g/L. The adsorption time was always 20 h. Subsequently, the suspension was centrifuged for 10 min at 5000 rpm, the supernatant was rejected, and the centrifugate was washed for 5 min with $CHCl_3$ and centrifuged again.

Sample Preparation and ESR Measurements. A suspension of the washed centrifugate in 5 mL of $CHCl_3$ was filled in a standard ESR quartz tube ($d = 2$ mm) and measured at room temperature. Temperature dependent measurements with the pure polymers and the polymers adsorbed on Aerosil 200 were carried out with the samples in the solid state in the same standard ESR tubes.

ESR spectra were measured in a rectangular cavity with the following parameters: sweep width, 100 G; time constant, 82 ms; sweep time, 168 s; number of scans, 1–3; modulation frequency, 100 kHz; microwave power, 5–15 mW; modulation amplitude, 0.5–2.0 G. (The variation of the microwave power and modulation amplitude in the mentioned range does not influence the line shape of the ESR spectra.[25])

ESR Model Spectra. (i) The "tail"/"long loop" model spectrum is a spectrum of a dilute solution of the labeled polymer in $CHCl_3$ at room temperature. (ii) The "short loop" model spectrum is a spectrum of a highly viscous solution of the labeled polymer (25 wt % polymer) in $CHCl_3$ at room temperature. (iii) The "train" model spectrum is a spectrum of a dilute solution of the labeled polymer in $CHCl_3$ at 153 K. The model spectra are normalized by signal intensities obtained from the second integration of the first derivative spectra. The simulations of the measured spectra were carried out by weighted summation of the model spectra on a Bruker ESP 300E computer configuration.

Determination of the Adsorption Isotherms. The thermogravimetric analysis was used to determine the adsorbed mass of polymer in g/m^2.[33] Samples with different surface converages were dried in vacuo until they reached a constant weight and were then subjected to TG analysis in the temperature range 298–1173 K with a heating rate of 10 K/min in a crucible of aluminum oxide. The weight loss is equal to the adsorbed polymer mass since pure Aerosil 200 shows no weight loss in this temperature range.

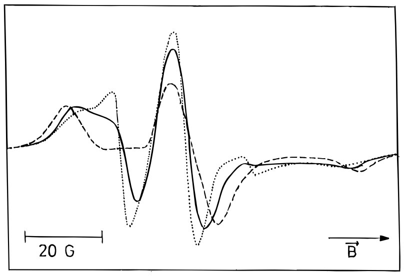


Figure 1. ESR model spectra for PODMA in $CHCl_3$: (···) model spectrum for "tails/long loops" (dilute solution of the spin-labeled polymer at 298 K); (—) model spectrum for "short loops" (25 wt % solution of the spin-labeled polymer at 298 K); (- - -) model spectrum for "trains" (dilute solution of the labeled polymer at 153 K).

The equilibrium polymer concentration in the supernatant was calculated from the difference of the polymer mass in the feed and the mass of adsorbed polymer.

Results and Discussion

Spin Labeling of the Polymers. ESR Model Spectra. For the polymer systems investigated the nitroxide 4-amino-TEMPO (**3**) is the most suitable spin label. The free amino group of the spin label reacts easily with a maleic anhydride group of PODMA (**1**) at room temperature under formation of an amide (Scheme 1, eq 1), whereas PDDMAM(EO)$_7$Me (**2**) with free carboxylic acid groups reacts with the amine group of the spin label in the presence of an equimolar amount of DCC as an activating coupling agent (eq 2).

In this way, spin-labeled PODMA and PDDMAM(EO)$_7$Me were obtained (as the ESR model spectra reveal), which were used for adsorption on Aerosil 200. The TGA behavior and the adsorption isotherms of the labeled polymers were identical with those of the unlabeled polymers. Model spectra for "tails"/"long loops", "short loops", and "trains" (Figures 1 and 2) reveal a gradual decrease in the mobility of the spin label in the transition from the model spectra for "tails"/"long loops" to the model spectra of "trains". We decided to change the conditions for the model spectrum for "short loops" by working in a highly viscous polymer

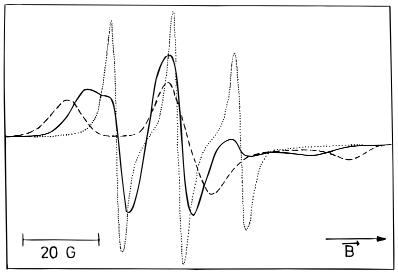


Figure 2. ESR model spectra for PDDMAM(EO)$_7$Me in CHCl$_3$: (···) model spectrum for "tails/long loops" (dilute solution of the spin-labeled polymer in CHCl$_3$ at 298 K); (—) model spectrum for "short loops" (25 wt % solution of the spin-labeled polymer at 298 K); (- - -) model spectrum for "trains" (dilute solution of the spin-labeled polymer at 153 K).

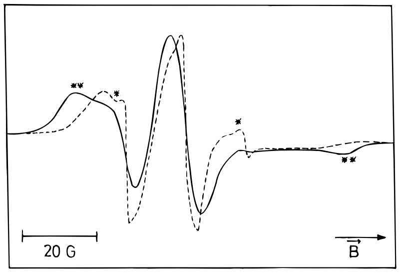


Figure 3. Comparison of the model spectra for "short loops" for PODMA: (- - -) spin-labeled PODMA in the molten state; (—) spin-labeled PODMA in CHCl$_3$ (25 wt % solution) at room temperature.

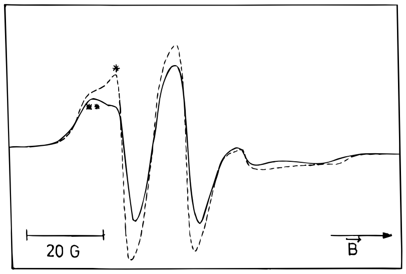


Figure 4. Comparison of the model spectra for "short loops" for PDDMAM(EO)$_7$Me: (- - -) spin-labeled PDDMAM(EO)$_7$Me in the molten state; (—) 25 wt % solution of spin-labeled PDDMAM(EO)$_7$Me in CHCl$_3$ at room temperature.

solution (25 wt % polymer) at room temperature instead of the polymer melt, wheras the conditions for the model spectra for "tails"/"long loops" and "trains" were retained.[19] As shown in Figures 3 and 4 the model spectra of the highly viscous solutions indicate a greater restriction in the mobility of the spin label than in the molten state. Since the determination of the conformation of adsorbed polymer chains by means of ESR spectroscopy following the method of Sakai et al. overestimates the fraction of polymer segments in "trains" compared with results obtained from IR spectroscopic measurements, the above modification of the model spectrum for "short loops" is expected to give a better agreement with the IR method.

Adsorption Isotherms of PODMA and PDDMAM(EO)$_7$Me. The adsorption isotherms of PODMA and PDDMAM(EO)$_7$Me (Figure 5) initially rise steeply and reach a plateau region with increasing equilibrium polymer concentration. The shape of the isotherms is of the high-affinity type with a steep slope at low, and a plateau region at high, equilibrium concentrations, a typical shape of the adsorption isotherms of polymers.[34,35] The concentration maximum of the adsorbed mass was found to be 1.1 mg/m^2 for PODMA and 1.0 mg/m^2 for PDDMAM(EO)$_7$Me. Plateau values of this order are reported for many homo- and copolymers at the state of monolayer adsorption.[36,37] Ideal high-affinity isotherms are only found for very low polydispersities $M_w/M_n < 1.01$. PODMA with a polydispersity of $M_w/M_n = 1.8$ and PDDMAM(EO)$_7$Me with a polydispersity $M_w/M_n = 3.7$ show appropriate isotherms, the transition into the plateau region being "more rounded" compared to the ideal shape.

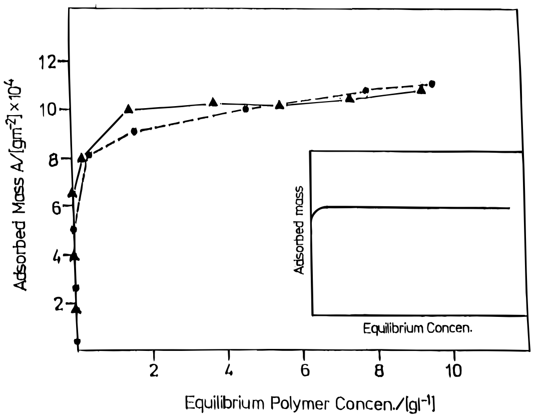


Figure 5. Adsorption isotherms of PODMA (●) and PDDMAM(EO)$_7$Me (▲) on Aerosil 200 in CHCl$_3$ at 298 K: (- - -) ideal "high affinity" isotherm. The isotherm was determined via TGA.

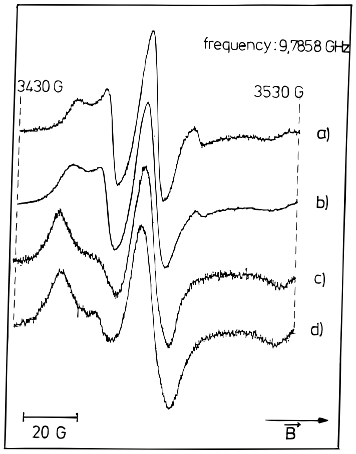


Figure 6. ESR spectra of adsorbed PODMA on Aerosil 200 in CHCl$_3$ at 298 K: (a) $\Theta = 1$; (b) $\Theta = 0.60$; (c) $\Theta = 0.25$; (d) $\Theta = 0.13$.

Conformation of the Adsorbed Polymer Chains Determined via ESR Spectroscopy. Figure 6 shows the ESR spectra of adsorbed PODMA at different surface coverages Θ ($\Theta = A/A_\infty$, with A = amount of polymer in g/m^2 Aerosil 200 and A_∞ = amount of polymer in q/m^2 Aerosil 200 in the plateau region of the adsorption isotherm). At the transition from high to low surface coverage (Figure 6a−d) the line shapes of the ESR spectra of adsorbed PODMA gradually become broader, which indicates a significant change in the conformation of the adsorbed polymer chains. The ESR signals from the nitroxide label attached to the polymer chain reflect sensitively the changes in the motion of the adsorbed chain segments arising from the differences in the configurational states.

To determine the fraction of adsorbed chain segments in "tails"/"long loops", "short loops", and "trains", the line shapes of the measured spectra in Figure 6 were simulated by weighted summation of the three model spectra. Figure 7 shows the result of the simulated

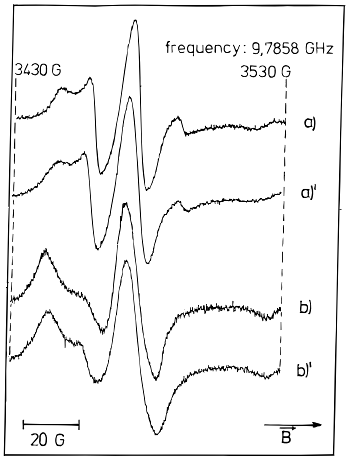


Figure 7. Comparison of measured and simulated ESR spectra of PODMA adsorbed on Aerosil 200 in $CHCl_3$: (a) measured spectrum for $\Theta = 1$; (a′) simulated spectrum for $\Theta = 1$; (b) measured spectrum for $\Theta = 0.25$; (b′) simulated spectrum for $\Theta = 0.25$.

Table 1. Segment Fraction (%) of Adsorbed PODMA on Aerosil 200 in $CHCl_3$ at 298 K in the conformation of “Tails/Long Loops”, “Short Loops”, and “Trains”

Θ^a	“tails/long loops”	“short loops”	“trains”
0.11	4.5	22.0	73.5
0.23	12.5	25.0	62.5
0.33	43.0	36.0	21.0
0.45	48.0	37.0	15.0
0.55	69.0	21.0	10.0
0.68	73.0	20.0	7.0
0.82	74.0	19.5	6.5
1	74.5	19.5	6.0

[a] $\Theta = A/A_\infty$ where A = g of polymer/m^2 Aerosil 200 and A_∞ = g of polymer/m^2 Aerosil 200 in the plateau region of the adsorption isotherm.

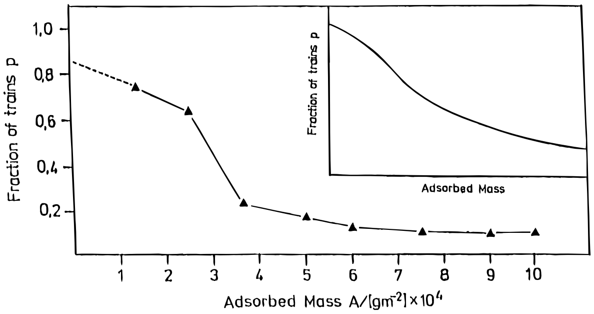


Figure 8. Fraction of “trains” (p) as a function of the adsorbed mass: (▲) experimental results for PODMA; (—) result of the SF theory.

spectra exemplarily in direct comparison with the line shape of the measured spectra. Simulated (Figure 7a′,b′) and measured spectra (Figure 7a,b) are in good agreement. The conformation of PODMA at different degrees of surface coverage in terms of fractions of segments in “tails”/“long loops”, “short loops”, and “trains” is summarized in Table 1. With increasing surface coverage a strong shift from “train” to ”tail”/“long loop” conformation occurs. The theoretical prediction of Scheutjens and Fleer (SF Theory, Figure 8) for the “train”—“loop”—“tail” distribution correlates with these experimental results. The SF theory implies that the conformational parameters—the fraction of polymer segments in the conformation of “tails”, “loops”, and “trains”—are a function of the adsorbed mass. The theory delivers a characteristic dependence of the fraction of adsorbed polymer segments in “trains” (p) on the adsorbed mass.[5,36] Figure 8 shows that the fraction of trains (p) decreases with increasing adsorbed mass. The theoretical prediction fits the experimental results very well.

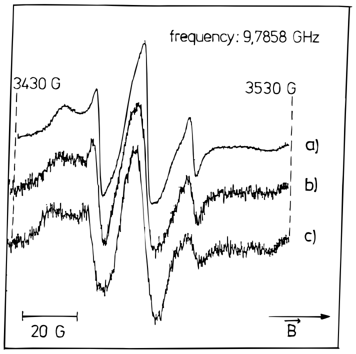


Figure 9. ESR spectra of adsorbed PDDMAM(EO)$_7$Me on Aerosil 200 in $CHCl_3$ at 298 K: (a) $\Theta = 1$; (b) $\Theta = 0.30$; (c) $\Theta = 0.20$.

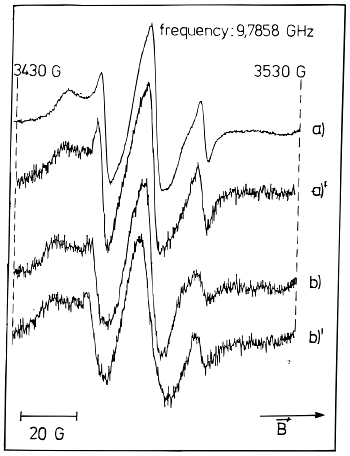


Figure 10. Comparison of measured and simulated ESR spectra of PDDMAM(EO)$_7$Me adsorbed on Aerosil 200 in $CHCl_3$: (a) measured spectrum for $\Theta = 1$; (a′) simulated spectrum for $\Theta = 1$; (b) measured spectrum for $\Theta = 0.2$; (b′) simulated spectrum for $\Theta = 0.2$.

Table 2. Segment Fraction (%) of Adsorbed PDDMAM(EO)$_7$Me on Aerosil 200 in $CHCl_3$ at 298 K in the Conformation of “Tails/Long Loops”, “Short Loops”, and “Trains”

Θ^a	“tails/loop loops”	“short loops”	“trains”
0.19	5.0	32.0	63.0
0.30	8.5	30.5	61.0
0.40	9.0	30.0	61.0
0.80	11.5	29.5	59.0
1	12.0	29.0	59.0

[a] $\Theta = A/A_\infty$ where A = g of polymer/m^2 Aerosil 200 and A_∞ = g of polymer/m^2 Aerosil 200 in the plateau region of the adsorption isotherm.

The ESR spectra of PDDMAM(EO)$_7$Me adsorbed on Aerosil 200 are not indicating a significant change in the conformations of the adsorbed polymers at the transition from high to low surface coverage (Figure 9a—c). The line shapes of the spectra are nearly identical.

The results of the simulations—two examples of simulated spectra are shown in Figure 10—with respect to the conformations of the polymer chains at different degrees of surface coverage are summarized in Table 2. With increasing surface coverage Θ ($\Theta = A/A_\infty$, with A = amount of polymer in g/m^2 Aerosil 200 and A_∞ = amount of polymer in g/m^2 Aerosil 200 in the plateau region of the adsorption isotherm), the fraction p of

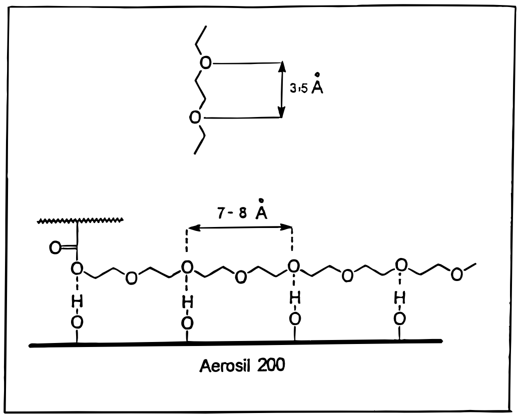


Figure 11. Schematic representation of the interaction of heptakis(ethylene oxide) side chains of PDDMAM(EO)$_7$Me with four silanol groups of Aerosil 200.

polymer segments adsorbed in "trains" does not decrease significantly and likewise a small increase of the fraction of "tails"/"long loops" is observed. The conformations of the adsorbed polymer chains apparently do not change with the degree of coverage. This result is in contrast to the results obtained for the PODMA polymers in the adsorbed state. The reason for this different behavior of the two polymers with respect to their conformation on the Aerosil 200 particles is in our opinion their different chemical structures. Both polymers consist of alternating hydrophilic and hydrophobic segments. The hydrophobic segments of the copolymers are very similar—hydrocarbon chains of different lengths—C_{16} for PODMA and C_{10} for PDDMAM(EO)$_7$Me; however, the quality of the hydrophilic segments differs significantly. While in PODMA the maleic anhydride segments are the only hydrophilic groups, in PDDMAM(EO)$_7$Me two different hydrophilic groups are present: (i) the protic hydrophilic carboxyl group and, (ii) the aprotic hydrophilic heptakis(ethylene oxide) side chain. The adsorptive interactions of both polymers take place between the hydrophilic polymer segments and the free silanol groups of the surface of Aerosil 200. While a maleic anhydride unit may interact with only one hydroxyl group of the Aerosil 200 particles, a heptakis(ethylene oxide) side chain may interact with 1−4 hydroxyl groups of the Aerosil 200 particles, as was concluded from literature data[38−42] (Figure 11). Schematically, the adsorbed polymers on Aerosil 200 suspended in chloroform are shown as a function of the surface coverage and the particle concentration (Figures 12 and 13). For PODMA the model clearly suggests an increase of the segment mobility with increasing surface coverage (Figure 12a,a′). This mobility is reduced when the particles come closer due to a higher particle concentration (Figure 12b). In contrast PDDMAM(EO)$_7$Me suggests no increase in mobility of the chain segments at higher surface coverages, since the "tails" and "long loops" of this polymer aggregate in chloroform solution to give micelle-like structures in which the individual mobility is lost (Figure 13a,a′). At a higher particle concentration no additional loss in mobility is expected (Figure 13b).

As a consequence of this schematic model, the description of the conformation of PDDMAM(EO)$_7$Me in the adsorbed state in "trains", "short loops", and "tails/long loops" (according to the method of Sakai et al.) is out of proportion. The immobilization of PDDMAM(EO)$_7$Me is caused by the density of the EO side chains on the surface, while the spin labels are attached to the polymer backbone and are not in contact with the surface. Under this aspect the results of the simulation

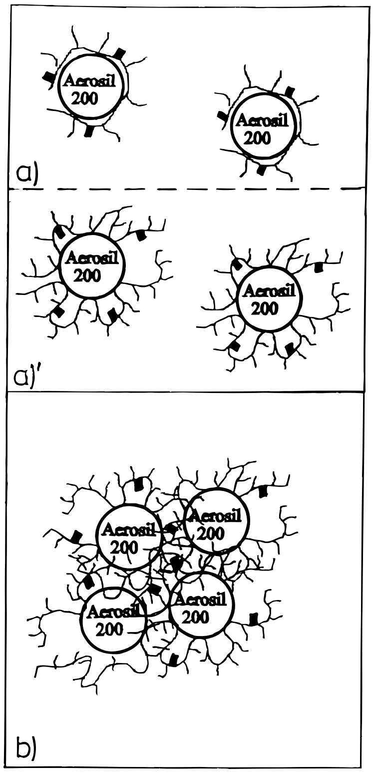


Figure 12. Schematic view on the Aerosil 200 particles coated with PODMA: (a) suspension of particles at low surface coverage; (b) suspension of particles at high surface coverage; (c) centrifuged suspension of particles at high surface coverage. (■, spin label.)

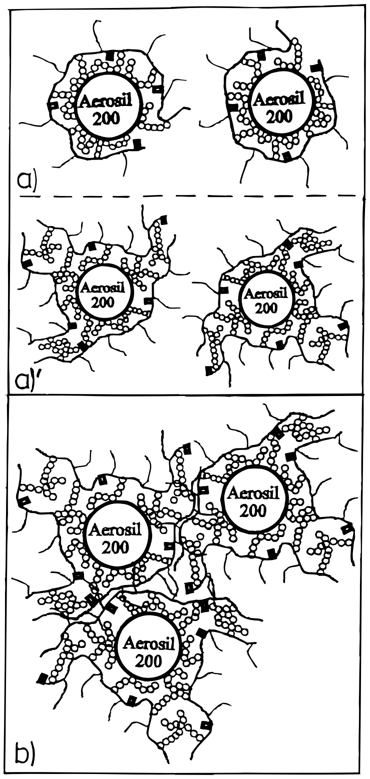


Figure 13. Schematic view on the Aerosil 200 particles coated with PDDMAM(EO)$_7$Me: (a) suspension of particles at low surface coverage; (b) suspension of particles at high surface coverage; (c) centrifuged suspension of particles at high surface coverage. (■, spin label; ooo, poly(ethylene oxide) chains.)

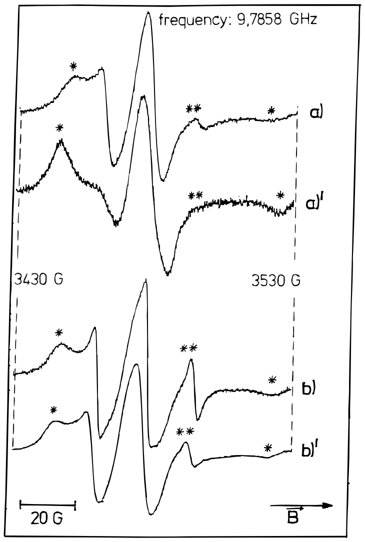


Figure 14. ESR spectra of the centrifuged suspensions compared with the spectra in suspension: (a) PODMA adsorbed on Aerosil 200 $(\Theta = 1)$ in suspension; (a′) PODMA adsorbed on Aerosil 200 $(\Theta = 1)$ centrifuged suspension; (b) PDDMAM(EO)$_7$Me adsorbed on Aerosil 200 $(\Theta = 1)$ in suspension; (b′) PDDMAM(EO)$_7$Me adsorbed on Aerosil 200 $(\Theta = 1)$ centrifuged suspension.

of the conformation of PDDMAM(EO)$_7$Me on Aerosil/200 represented in Table 2 are restricted in the way that the method of Sakai et al. does not deliver a realistic conformation for this kind of polymer.

The result of the following experiments supports this schematic view. A suspension of Aerosil 200 particles covered with adsorbed polymer $(\Theta = 1)$ was centrifuged with 5000 rpm, and the supernatant was rejected. For the remaining particles coated with PODMA the ESR spectrum (Figure 14a′) shows a line broadening and a decreasing height of the high-field line in comparison to the ESR spectrum in suspension (Figure 14a). This indicates a restriction of the chain mobility with increasing particle concentration. For the remaining particles coated with PDDMAM(EO)$_7$Me (Figure 14b′) the line shape of the ESR spectrum shows no line broadening and only a small decrease of the height of the high-field line in comparison to the ESR spectrum in suspension (Figure 14b).

Conclusion

According to the chemical structure of the polymers PODMA and PDDMAM(EO)$_7$Me the adsorption at the Aerosil 200 particles leads to a substantial difference of the conformations of the adsorbed polymer chains.

PODMA shows a drastic decrease of the fraction p of polymer segments adsorbed in "trains" with increasing surface coverage. In this case the theory of Scheutjens and Fleer is in agreement with the experimental results and the method of Sakai et al. can be applied for the evaluation of the conformation of adsorbed polymers. PDDMAM(EO)$_7$Me, however, hardly indicates a change of the conformation as a function of surface coverage. PODMAM(EO)$_7$Me builds up a micelle-like structure in the adsorbed state due to the long hydrophilic heptakis(ethylene oxide) side chains and the hydrophobic C$_{10}$ side chains. Hence, the method of Sakai et al. cannot be applied to this polymer to evaluate the chain conformation in the adsorbed state.

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